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We have concentrated our efforts on the spectroscopy, photophysics, and photochemistry of polysilanes, using a combination of experimental and theoretical tools. We have developed a more detailed version of the chain segment model, have identified and thoroughly characterized the persistent radical formed in UV photolysis, documented further the recently uncovered process of photoinduced chain scission by reductive elimination, and advanced the theoretical understanding of the electronic states of model short-chain oligosilanes. The combined results suggest strongly that the shorter chromophoric chain segments have a different lowest excited singlet state (σπ*) than the longer ones (σσ*). Confirming evidence for this is still being sought.

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Technical Report

# STRUCTURE AND PROPERTIES OF NOVEL COMPOUNDS OF SILICON, GERMANIUM AND TIN

The Air Force Office of Scientific Research
Air Force Systems Command

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## ABSTRACT

We have concentrated our efforts on the spectroscopy, photophysics, and photochemistry of polysilanes, using a combination of experimental and theoretical tools. We have developed a more detailed version of the chain segment model, have identified and thoroughly characterized the persistent radicals formed in UV photolysis, documented further the recently uncovered process of photoinduced chain scission by reductive elimination, and advanced the theoretical understanding of the electronic states of model short-chain oligosilanes. The combined results suggest strongly that the shorter chromophoric chain segments have a different lowest excited singlet state ($\sigma\pi^*$) than the longer ones ($\sigma\sigma^*$). Confirming evidence for this is still being sought.

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The following individuals participated in the work:

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CUMULATIVE LIST OF PUBLICATIONS WHICH ACKNOWLEDGE SUPPORT OF AFOSR 87-0001

A. **Publications previously reported:**


1. Michalczyk, M. J.; Fink, M. J.; Haller, K. J.; West, R.; Michl, J. "Structural and Chemical Properties of 1,3-Cyclodisiloxanes", *Organometallics* 1986, *5*, 531.

2. Michalczyk, M. J.; Fink, M. J.; De Young, D. J.; Carlson, C. W.; Welsh, K. M.; West, R.; Michl, J. "Organosilylenes and their Dimerization to Disilenes", *Silicon, Germanium, Tin, and Lead Compounds* 1986, *9*, 75.

3. Vančik, H.; Raabe, G.: Michalczyk, M. J.; West, R.; Michl, J. "Dimethylsilylene: A Trisilane and a Geminal Diazide as New Photochemical Precursors. Evidence for an Absorption Maximum Near 450 nm", *J. Am. Chem. Soc.* 1985, *107*, 4097.

4. Weeks, G. H.; Adcock, W.; Klingensmith, K. A.; Waluk, J. W.; West, R.; Vasak, M.; Downing, J.; Michl, J. "A Probe for Substituent Hyperconjugative Power: Magnetic Circular Dichroism of the Benzene $L_b$ Band", *Pure Appl. Chem.* 1986, *58*, 39.

5. Raabe, G.; Vančik, H.; West, R.; Michl, J. "IR Transition Moment Directions in Matrix-Isolated Dimethylsilylene and 1-Methylsilene", *J. Am. Chem. Soc.* 1986, *108*, 671.

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11. Raabe, G.; Michl, J. "Multiple Bonding to Silicon", *Chem. Rev.* 1985, *85*, 419.

12. Welsh, K. M.; Michl, J.; West, R. "The Photochemistry of Matrix-Isolated Di-*tert*-butyldiazidosilane. Observation of Di-*tert*-butylsilylene and N,N'-Di-*tert*-butylsilanediimine", *J. Am. Chem. Soc.* 1988, *110*, 6689.

13. Raabe, G.; Michl, J. "Multiple Bonds to Silicon", in "The Chemistry of Organic Silicon Compounds", Patai, S.; Rappoport, Z., Eds., John Wiley & Sons Ltd.: Chichester, 1989, Chapter 17, 1015.

B. **Publication previously reported as in Press or Submitted that have now appeared:**

14. Barrau, J.; Bean, D. L.; Welsh, K. M.; West, R.; Michl, J. "Photochemistry of a Matrix-isolated Geminal Diazide: Dimethylgermylene", *Organometallics* 1989, *8*, 2606.

15. Barrau, J.; Balaji, V.; Michl, J. "Matrix Isolation and IR Spectroscopy of Germanethione $Me_2Ge{=}S$", *Organometallics*, 1989, *8*, 2034.

16. Radziszewski, J. G.; Michl, J. "Doubled Multiplexing in Fourier Transform Raman Spectroscopy", *J. Appl. Spectrosc.* 1990, *44*, 414.

17. Michl, J., "The Relationship of Bonding to Electronic Spectra", *Acc. Chem. Res.* 1990, *23*, 127.

C. **Publications submitted since the last report was written:**

18. Sun, Y.-P.; Miller, R. D.; Sooriyakumaran, R.; Michl, J. "Fluorescence of Poly(di-*n*-alkylsilane)s in Room-Temperature Solution", *J. Inorg. Organomet. Polym.*, in press.

19. McKinley, A. J.; Karatsu, T.; Wallraff, G. M.; Thompson, D. P.; Miller, R. D.; Michl, J. "Solution Photochemistry of Poly(di-*n*-alkylsilane)s. An EPR-ENDOR Study of the Structure of the Persistent Radicals", *J. Am. Chem. Soc.*, in press.

20. Davidson, I. M. T.; Michl, J.; Simpson, T., "The Photochemistry of Some Permethyloligosilanes", submitted for publication.

21. Michl, J.; Balaji, V., "Calculations of Photochemical Reactivity. Oligosilanes as an Illustration" in *Computational Advances in Organic Chemistry*; Ögretir, C., Csizmadia, I. G., Eds.; Kluwer: Dordrecht, The Netherlands; in press.

22. Balaji, V.; Michl, J. "Singlet Excitation in Polysilanes: *Ab initio* Calculations on Oligosilane Models", *Polyhedron*, in press.

23. Miller, R. D.; Michl, J. "Polysilane High Polymers", *Chem. Rev.* 1989, *89*, 1359.

24. Miller, R. D.; Wallraff, G.; Clecak, N.; Sooriyakumaran, R.; Michl, J.; Karatsu, T.; McKinley, A. J.; Klingensmith, K. A.; Downing, J., "Polysilanes: Solution Photochemistry and Deep UV Lithography", *Polym. Eng. Sci.* 1989, *29*, 882.

## SCIENTIFIC RESULTS

In this period, our work has emphasized oligosilanes and polysilanes, reflecting the intense interest in this area among chemists, physicists and material scientists. We have concentrated on the fundamental aspects (nos. 18-23 on the list of references) but participated also in the exploitation of these materials for deep UV lithography (no. 24 on the list).

We have performed a comprehensive study [18] of the luminescence of polysilanes in room-temperature solution and proposed an improved version of the chain segment model that we published in 1986. We have completed an extensive investigation [19] of the persistent radicals formed by UV irradiation of polysilane solutions and determined their structure, including conformational properties, by EPR, ENDOR, and TRIPLE resonance on a series of isotopically labeled polymers. These now probably are the best characterized polymer-based radicals of any kind. We have proposed plausible mechanisms for the complex chemical transformations involved in the formation of the observed radical products, and assigned a key role to photoinduced chain scission by homolysis and by reductive elimination; while the former had always been taken for granted, we postulated the latter only in 1989. We have now found confirming evidence for the latter from a study of the photochemistry of short-chain oligosilanes [20]. It has thus become clear that at least three primary processes are important in the photodegradation of polysilanes: the two types of chain scission, and the chain abridgement by silylene extrusion, described by Trefonas, West and Miller in 1985.

We have obtained satisfactory theoretical descriptions of all three primary processes by means of *ab initio* computations on model oligosilanes [21]. We have used this theoretical tool to investigate the excited electronic states in fair amount of detail [21, 22] and obtained a picture in which the photophysical and photochemical results dovetail. In particular, we have obtained evidence suggesting that a switch in the order of states occurs at chain lengths of about $Si_6$ to $Si_{10}$. Shorter chains are believed to have a $^1\sigma\pi^*$ state and the longer ones a $^1\sigma\sigma^*$ state as the lowest excited singlets with obvious implications for spectroscopy, photophysics, and photochemistry. However, although reasonably advanced, the degree of understanding of these fascinating materials is still far from complete and the work is being continued. The current state of knowledge has been summarized in a comprehensive review [23].

In addition to results that have already been submitted for publication, further results are still being analyzed now. In particular, although some of the mysteries of the photophysics of oligosilanes have been resolved (e.g., what appeared to be a low-temperature conformational form of $Si_{16}Me_{34}$ was demonstrated to be due to an aggregate which forms even in highly dilute solutions - true conformational effects have now also been found), several baffling observations remain to be explained, and in collaboration with Prof. West, we are continuing our efforts to understand simple model compounds such as $Si_{16}Me_{34}$.